reduced, the melt color varied from red to deep red and a new redox couple, together with the redox peaks of the $Ru(acac)_3/Ru(acac)_3^-$ couple, appeared at −0.01 V in the cyclic voltammogram; here the potential in pure ImCl melt is converted to the potential against the Al/Al(III) reference electrode in the 1.5:1.0 melt at 30 °C using the redox potential of $Ru^{III}(acac)_3/Ru^{II}(acac)_3^-$ as an internal standard. The color and cyclic voltammogram of the melt did not change after it was left overnight at 100 °C. These results strongly suggest that $AlCl_4^-$ in the melt induces the ligand exchange of $Ru^{III}(acac)_3$ to form $Ru^{III}Cl_6^{3-}$.

Other acac Complexes. $Fe(acac)_3$ dissolved in the basic melt; however, it decomposed almost immediately to form the $FeCl_4^-$ complex, as indicated by the half-wave potential and spectrum.[37]

$Co(acac)_3$ gave an irreversible reduction wave in a 0.8:1.0 melt; the cathodic peak potential in a CS voltammogram shifted from −0.48 to −0.58 V as the scan rate varied from 0.02 to 0.5 V s^{-1}. The values of λ_{max} from UV–vis spectroscopy of 259 and 328 nm were in good agreement with those for this complex in acetonitrile, 258 and 324 nm, respectively, previously reported.[11] The diffusion coefficient was evaluated from NP voltammograms, assuming a one-electron reduction. For a solution containing 7.8 mmol dm^{-3}, a D value of 1.8×10^{-7} cm^2 s^{-1} and an r value of 0.41 nm were calculated; these are very similar to the values found for the $Ru(acac)_3$ complexes and are similar to those found in acetonitrile solutions.[20] This complex was not investigated further.

Acknowledgment. This work was supported by the Air Force Office of Scientific Research. Helpful discussions with other members of our research group and with Prof Charles Hussey are also acknowledged.

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Observation of Radical Intermediates for Unusual C–N Bond Formation of α-Aminomalonate To Give an α-Diamine Linkage. ESR Studies on Electron Transfer Reactions in Cobalt(III)–Polyamine Complexes

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Received December 20, 1991

The reactions of α-aminomalonate anion (AM^{2-}) with complexes *trans*-$[Co^{III}Cl_2(N_4)]^+$ (N_4 = $(en)_2$, 2,3,2-tet, 3,2,3-tet; en = ethylenediamine, 2,3,2-tet = 3,7-diaza–1,9-diaminononane, 3,2,3-tet = 4,7-diaza-1,10-diaminodecane) were investigated by spin trapping and low-temperature electron spin resonance (ESR) spectroscopy. In the thermal C–N bond formation between the α-carbon of AM^{2-} and a coordinated amino group of polyamine ligands, pathways for oxidation of AM^{2-} to an iminomalonato intermediate depend on polyamine systems. Spin-trap ESR spectroscopy showed that the oxidation of AM^{2-} proceeds via the radical formation at the α-carbon in the en and 2,3,2-tet systems. In both systems, MeOH plays an indispensable role in the α-diamine formation. Especially in the en system, the radicalization of MeOH took place upon heating prior to that of AM^{2-} accompanying electron transfer (ET) to give a d^7 high-spin ($S = {}^3/_2$) Co(II) species from a d^6 low-spin Co(III) ion. This change of the spin state at the cobalt center is required when a Co(III) complex acts as an oxidant for AM^{2-}. In contrast, in the 2,3,2-tet system, the Co(III) center was reduced upon heating toward a low spin ($S = {}^1/_2$) Co(II) species which readily reacted with dioxygen in the air to give a $Co^{III}–O_2^-$ complex. EHMO calculation suggested that the superoxo ligand can perform intramolecular deprotonation of the α-proton of AM^{2-} ligand and ET can occur from the α-carbon of the AM^{2-} ligand to the Co(III) center. In the 3,2,3-tet system, formation of a high-spin Co(II) species was observed like the en system under conditions where the α-diamine formation occurs via ET from AM^{2-} to a Co(III) ion. For the oxidation of substrates by Co(III) complexes via ET, the change of the spin state at the cobalt center is important and it is controlled by the polyamine ligands.

Introduction

The oxidation of organic compounds by transition-metal complexes has been intensively investigated in the light of not only industrial benefits but also modeling metalloenzymatic systems for elucidation of their functions and mechanisms, in which radical intermediates are often involved.[1] The oxidation processes catalyzed by transition-metal complexes include activation of substrates and/or reactants and often involve electron transfer (ET) reactions from the substrates to the metal centers.[2]

The oxido-reductases which contain metal ions in their active sites or flavin adenine dinucleotide (FAD) as a cofactor require dioxygen for the oxidation of substrates. In those reactions radical intermediates have been detected and proposed.[3b,4c,d] Thus, the action of these enzymes brings attention to dioxygen activation. For example, the well-reported observations of dioxygen activation in cytochrome P-450 systems have been integrated and the reaction mechanism has become the subject of much interest in chemistry.[5] For the reaction catalyzed by cytochrome P-450 systems and their models, radical intermediates have been also proposed and detected.[6] In addition, Nishinaga and Drago and their co-workers

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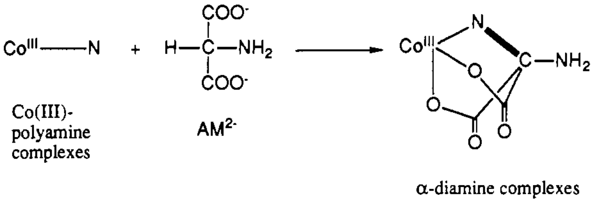
have reported the dioxygen activation by Co(II)–Schiff base complexes toward many kinds of oxidation and oxygenation reactions. In those reactions, they depicted dioxygen reduced to superoxide anion radical ($O_2^{\cdot-}$) by Co(II) ions at the opening step followed by the radical mechanism.[7] Nishinaga and co-workers also have reported the dehydrogenation of aniline derivatives through the radical formation of substrates involving ET to active Schiff base–Co^{III}–OH complexes in protic solvents.[8]



We have reported the reactions of α-aminomalonate anion (AM^{2-}) with cobalt(III)–polyamine complexes to give α-diamine and carbinolamine complexes, both of which have a new C–N bond between an amino group of polyamine ligands and the α-carbon of AM^{2-}.[9–11] For those reactions, an iminomalonato intermediate derived from the oxidation of AM^{2-} has been proposed.[9a,b] The reactions of AM^{2-} with Co(III)–polyamine complexes also give oxamato and oxalato complexes as products of oxidative decarboxylation under similar conditions.[12] On the other hand, the reaction of AM^{2-} with $[CoCl_2(tren)]^+$ (tren = tris(2-aminoethyl)amine) gave a novel imidomalonato-bridged binuclear complex, in which AM^{2-} had been dehydrogenated to possess a deprotonated imino group, without α-diamine and carbinolamine formation.[13] In the course of our research, we have observed that different conditions depending on polyamine systems are required for the C–N bond formation; for instance, dioxygen is required in the 2,3,2-tet (3,7-diaza-1,9-diaminononane) system,[9] in contrast to the en (ethylenediamine)[10] and 3,2,3-tet (4,7-diaza-1,10-diaminodecane)[11] systems. In this paper we report on the oxidation mechanism of AM^{2-} in the en, 2,3,2-tet and 3,2,3-tet systems: The formation of various kinds of radical intermediates and Co(II) species derived from ET reactions were revealed by ESR spectroscopy.

Experimental Section

MeOH and NEt_3 (triethylamine) were dried over Mg and P_2O_5, respectively, and distilled before use. The complexes, *trans*-$[CoCl_2(en)_2]Cl\cdot2H_2O\cdot HCl$ (**1**) or *trans*-$[CoCl_2(en)_2]ClO_4$ (**1′**),[14] *trans*-$[CoCl_2(2,3,2\text{-tet})]ClO_4$ (**2**),[15] and *trans*-$[CoCl_2(3,2,3\text{-tet})]ClO_4$ (**3**)[16] were prepared according to published procedures. α-Aminomalonate monoammonium (NH_4AMH) was also prepared as described before.[10]

ESR Measurements. 1. Spin Trapping ESR. Commercially obtained POBN (α-(4-pyridyl 1-oxide)-*N*-*tert*-butylnitrone) (Aldrich) and MNP (2-methyl-2-nitrosopropane dimer) (Aldrich) were used as spin trapping reagents without further purification. The spectra were obtained with a JEOL FE-1X ESR spectrometer operated at 100 kHz modulation in the X-band at 25 °C or 77 K unless otherwise noted. The samples containing MNP were treated in the dark. Generally, 0.1 M solutions of the spin trap reagents and 1 aliquot of NEt_3 were added to the solid compounds which was a cobalt complex or NH_4AMH or a mixture of the two. Thermal reactions were performed under N_2 by heating for 30 min at 65–70 °C. Samples for photoinductive reactions were prepared by irradiation with an Hg lamp in the sample tubes. To prevent the loss of ESR spectral resolution due to dissolved molecular oxygen, the samples from reactions that were carried out under air were degassed by at least three freeze–pump–thaw cycles and sealed at ca. 10^{-4} Torr. Hyperfine coupling constants from the spectra were measured by using that of Mn^{2+} in MnO as a reference.

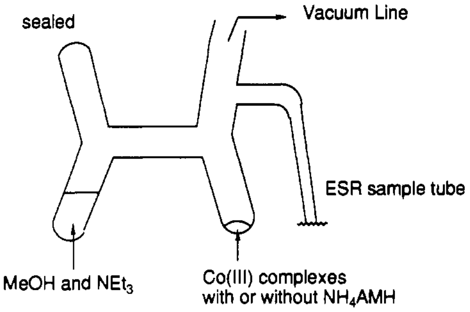


Figure 1. Preparing equipment of ESR samples for measurements at liquid He temperatures.

2. ESR Measurements at Liquid He Temperatures. The samples were prepared with an apparatus as shown in Figure 1. All starting complexes were confirmed by ESR spectroscopy that no Co(II) species were observed even at liquid He temperatures. Co(III) complexes and/or NH_4AMH were mixed at room temperature with $MeOH/NEt_3$ that underwent freeze–pump–thaw cycles under vacuum. After the apparatus was heated at about 70 °C for 2–3 h, the reaction mixtures were transferred to the sample tubes and they were sealed under vacuum. The spectra were obtained on a JEOL FE-3X ESR spectrometer operated at 100 kHz frequency modulation in the X band.

3. EHMO Calculations. The construction of an intermediate for the 2,3,2-tet system was made by using the positional parameters of $[Co(AM)(2,3,2\text{-tet})]ClO_4\cdot H_2O$[9c] and those of a superoxo Co(III) complex reported by Schaefer and co-workers[17] for a superoxo ligand: Co–O, 1.870 Å; O–O, 1.350 Å; Co–O–O, 116.4°. The construction of the hypothetical intermediate and rotation of a monodentate AM^{2-} ligand were performed by using the Chem 3D program. All EHMO calculations were performed by the "Extended Huckel Program", written by Kitaura et al., on a PC-9801 RA and Epson PC-386V. The parameters were taken from those reported by Hoffmann et al.[18]

Results and Discussion

Ethylenediamine System. In this system, as described previously,[10] the α-diamine formation between **1** and AM^{2-} took place in $MeOH/NEt_3$ upon refluxing even under inert atmosphere. Under N_2 atmosphere, the occurrence of the α-diamine formation is independent of photoirradiation: the reaction took place in the dark as well as in the daylight without change of product distribution and the yield of the α-diamine complex. These results indicate that the oxidation of AM^{2-} to form an iminomalonato intermediate does not involve any light-induced step and, thus, is a thermal ET to a Co(III) center ion in **1**.

On the other hand, MeOH plays an indispensable role in the α-diamine formation. The reaction of AM^{2-} with **1** in H_2O/NEt_3 (pH <10) under air gave a carbinolamine complex as a main product which had a newly formed C–N bond, $[Co(HM\text{-}en)(en)]^+$ ($[Co(N\text{-}(2\text{-aminoethyl})\text{-}\alpha\text{-amino-}\alpha\text{-hydroxymalonato})(en)]^+$).[10] However, the reaction in H_2O/NEt_3 (pH <10) under N_2 or in acetone/H_2O/NEt_3 under air gave $[Co(AM)(en)_2]^+$ as a main product in which AM^{2-} coordinates to the cobalt center through the amino group and one of the carboxyl groups without a new C–N bond. When other solvents such as ethanol or acetone were

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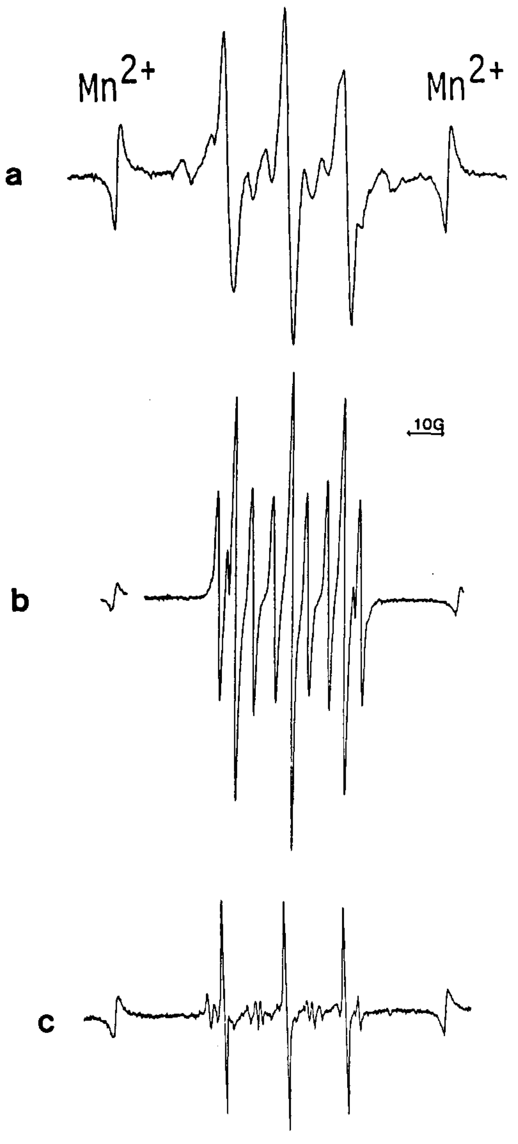


Figure 2. ESR spectra of MNP radical adducts observed under N_2 atmosphere: (a) MNP in $MeOH/NEt_3$ heated at 60–70 °C for 30 min; (b) **1** in $MeOH/NEt_3/MNP$ heated at 60–70 °C for 30 min; (c) NH_4AMH and **1** in $MeOH/NEt_3/MNP$ heated at 60–70 °C for 30 min. ESR spectrometer conditions: microwave power, 20 mW; modulation, 100 kHz, 0.5 G; scan range, 3280 ± 100 G; gain, (a) 4 × 1000, (b) 1 × 1000, (c) 2 × 1000. The phase-inverted signals of Mn^{2+} in MnO were used as calibrator of magnetic field and intensity.

used instead of MeOH, no α-diamine formation was observed. These results show that MeOH participates in the α-diamine formation.

1. Radicalization of Methanol. In order to reveal the necessity of MeOH as a solvent, spin trapping ESR spectroscopy was performed for the en system under an inert atmosphere. When only MNP (2-methyl-2-nitrosopropane dimer) was refluxed in $MeOH/NEt_3$, an ESR spectrum exhibited a weak triplet (a_N = 14.5 G, g = 2.006) attributed to the signal of $(t\text{-Bu})_2\text{–N–O}^\bullet$ derived from the thermolysis of MNP as shown in Figure 2a. When only **1** was refluxed in $MeOH/NEt_3/MNP$, an ESR spectrum of the reaction mixture showed as triplet of triplets (a_N = 14.2 G, $a_{H(2)}$ = 4.4 G, g = 2.007) ascribed to the signal of a spin adduct of $t\text{-Bu}(CH_2OH)\text{N–O}^\bullet$ derived from MeOH (Figure 2b).[19] This indicates that MeOH is radicalized by **1** and NEt_3 and also indicates that α-diamine formation occurs via a radical mechanism involving ET from an organic substrate, MeOH in this case, to a Co(III) ion of **1**. Conversely, under conditions where no products with a new C–N bond form, i.e. when **1** or **1** and NH_4AMH were heated to ca. 65 °C in $H_2O/NEt_3/MNP$ under N_2 atmosphere, no significant spin-adducts were observed by ESR spectroscopy. These results strongly suggest that the α-diamine formation, especially the oxidation of AM^{2-}, should proceed via a radical mechanism.

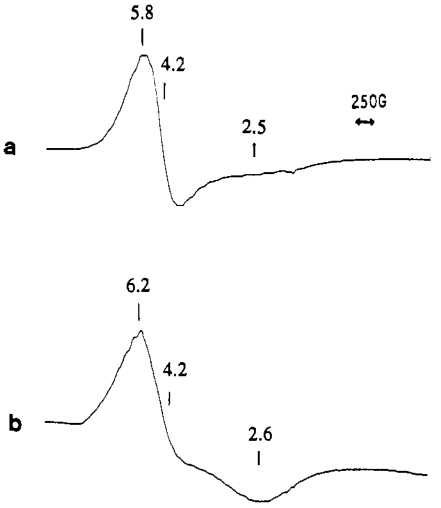
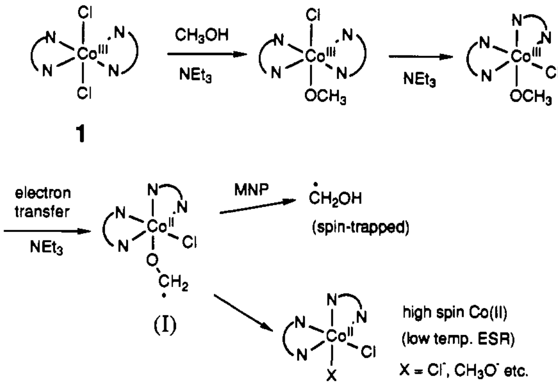


Figure 3. X-Band ESR spectra of the reaction mixtures at 4.2 K: (a) **1′** in $MeOH/NEt_3$ heated at 70 °C for 3 h in vacuo. (b) **1′** and NH_4AMH in $MeOH/NEt_3$ in vacuo. ESR spectrometer conditions: microwave power, 2 mW; modulation, 100 kHz, 10 G; scan range, 2500 ■ 2500 G; gain, (a) 7.9 × 10, (b) 5 × 10.

Scheme I



The occurrence of ET to a Co(III) ion in **1′** was confirmed by ESR spectroscopy at liquid He temperatures. No ESR signals were observed for **1′** in the solid state even at 4.2 K, confirming that a Co(III) ion in **1′** has a d^6 diamagnetic electronic structure. However, the ESR spectrum of the reaction mixture in which only **1′** had been heated at 60–70 °C in $MeOH/NEt_3$ in vacuo for 3 h showed a resonance at g_1 = 5.8, g_2 = 4.2, and g_3 = 2.5, as shown in Figure 3a. These g values are typical for a high-spin ($S = {}^3/_2$) Co(II) state.[20] This result indicates that the radicalization of methanol proceeds via deprotonation and then ET from a carbanion of methanol to the Co(III) in **1′**.

A proposed radicalization mechanism of MeOH in the en system is represented in Scheme I. A coordinated chloride around the Co(III) center is substituted by a CH_3O^- anion in a $MeOH/NEt_3$ system followed by trans to cis isomerization. Deprotonation of CH_3O^- ligand with NEt_3 and ET from $^-CH_2O^-$

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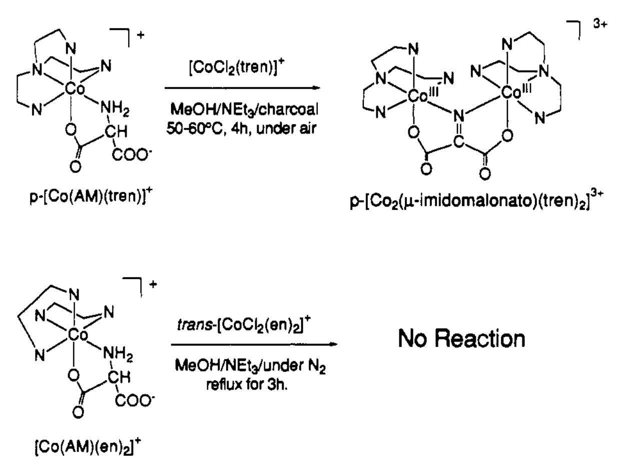
Scheme II



ligand to the Co(III) center results in the formation of a presumably unstable, labile, and undetected complex (I). For example, similar radical formation was previously suggested for coordinated nitriles in Co(III) complexes, caused by deprotonation followed by ET from a carbanion to the Co(III) center.[21] This Co(II) complex (I) then gives the observed high-spin Co(II) species which is assumed to be a byproduct as a result of ET reaction and a spin adduct of hydroxymethylene radical.

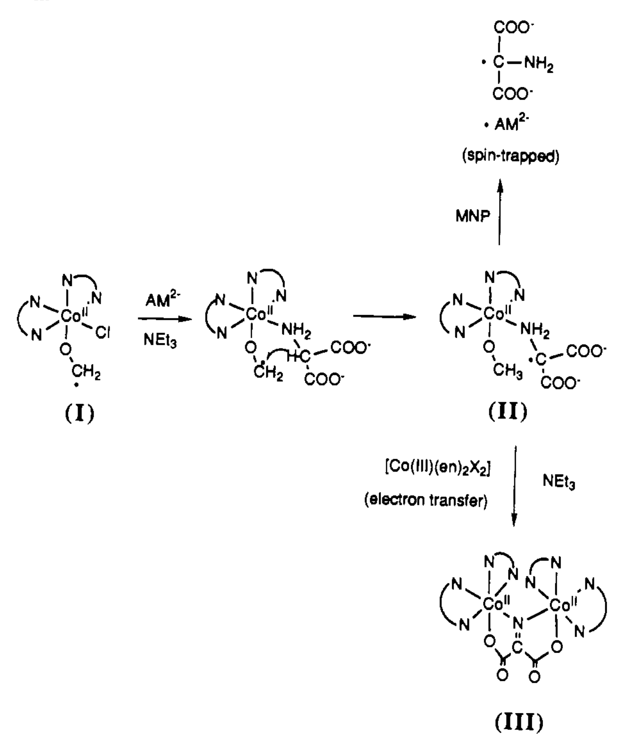
It has been reported that MeOH is dehydrogenated in the presence of acetone under UV irradiation with Rh catalysts and a radical intermediate ($^{\bullet}CH_2OH$) is postulated to form ethylene glycol and H_2.[22] However, in the reaction of the en system in MeOH/NEt$_3$, no radical coupling products were detected by gas chromatography (GC) even though the radical intermediate was observed. This result shows that the methanol radical intermediate is not released out of the coordination sphere but within that of the cobalt center. On the other hand, another dehydrogenation pathway is oxidative addition of a Ru catalyst to form formaldehyde via the so-called agostic interaction.[23] However, in our case, corresponding products were not detected by GC.

2. Oxidation of AM^{2-}. When both **1** and NH$_4$AMH were refluxed in MeOH/NEt$_3$ in the presence of MNP under N$_2$ atmosphere, an ESR spectrum of a spin adduct depicted in Figure 2c showed a triplet (a_N = 15.5 G, g = 2.006) with a different hyperfine coupling constant from that of $(t\text{-Bu})_2N\text{–}O^{\bullet}$ and was assigned to that of a spin adduct of a tertiary carbon radical, i.e. the α-carbon radical of AM^{2-}.

An ESR spectrum of a reaction mixture was obtained by heating **1′** and NH$_4$AMH at 65–70 °C under vacuum and then cooling the reaction mixture and measuring at 4.2 K. The spectrum shows a resonance at g_1 = 6.2, g_2 = 4.2, and g_3 = 2.6 assigned to another high-spin Co(II) species as represented in Figure 3b. This high-spin Co(II) species with AM^{2-} is the critical intermediate for the anomalous C–N bond formation to give the Co^{III}–α-diamine complex, i.e., a Co^{II}–α-diamine complex. The α-diamine linkage imposes severe steric constrains on the metal center that favors a high sign state for the Co^{II}–α-diamine complex.

When tren was used as an amine ligand, *p*-[Co(AM)(tren)]$^+$ reacted with [CoCl$_2$(tren)]$^+$ to form an imidomalonato-bridged binuclear Co(III) complex[13] in MeOH/NEt$_3$/charcoal at 50–60 °C for 4 h.[24] In contrast, the reaction of [Co(AM)(en)$_2$]$^+$ with **1** in MeOH/NEt$_3$ upon refluxing for 3 h resulted in giving no α-diamine complexes. Differences of the reactivity between two AM^{2-} complexes are summarized in Scheme II. Thus, this result clearly exhibits that [Co(AM)(en)$_2$]$^+$ with a bidentate AM^{2-} ligand is not an intermediate for the α-diamine formation. Therefore the C–N bond formation in the en system proceeds without formation of bidentate AM^{2-} complex. Later it will be shown that AM^{2-} coordinated to a Co(II) center as a monodentate ligand should undergo dehydrogenation to form the iminomalonato intermediate.

Scheme III



For all the reasons mentioned above, the oxidation mechanism of AM^{2-} in the en system is proposed as shown in Scheme III. The chloride in I is replaced by the amino group in AM^{2-}.[25] The intramolecular hydrogen abstraction from AM^{2-} ligand by the coordinated oxymethylene radical that locates in the cis position to the AM^{2-} ligand affords the observed captodative radical intermediate, i.e. the coordinated α-carbon radical of AM^{2-} (II).[26] Then, the excess NEt$_3$ abstracts an amino proton in the radical (II) and another Co(III) center accepts one electron to form a binuclear deprotonated iminomalonato intermediate (III), which is reasonably presumed from the structure of the complex obtained in the tren system as shown in Scheme II.[13]

Radical intermediates were previously proposed in the oxidation of amines and α-amino acids by an iron(III)–porphyrin system,[27] $[Fe(CN)_6]^{3-}$,[28] a Fremy's salt.[29] In those reactions, an α-ami-

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(25) In the tren system, the imidomalonato-bridged binuclear complex is obtained in only the p-isomer, which possesses a heteroatom (O) in the trans position to a primary amino group. In the complex, a nitrogen atom of the imdo group occupies the trans position to a tertiary amino group. Sargeson and co-workers showed that the first substitution occurs in the trans position to the tertiary amino group of a tren ligand. These observations indicate that the AM^{2-} ligand binds to a cobalt center in its amino group. See references: (a) Golding, B. T.; Harrowfield, J. M.; Sargeson, A. M. *J. Am. Chem. Soc.* **1974**, *96*, 3003. (b) Engelhardt, L. M.; Gainsford, A. R.; Gainsford, G. J.; Golding, B. T.; Harrowfield, J. M.; Herlt, A. J.; Sargeson, A. M. *Inorg. Chem.* **1988**, *27*, 4551.

(26) (a) de Vries, L. *J. Am. Chem. Soc.* **1978**, *100*, 926. (b) Viehe, H. G.; Merenyi, R.; Stella, L.; Janousek, Z. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 917. (c) Leigh, W. J.; Arnold, D. R. *Can. J. Chem.* **1981**, *59*, 609, 3061. (d) Dust, J. M.; Arnold, D. R. *J. Am. Chem. Soc.* **1983**, *105*, 1221. (e) Korth, H.-G.; Lommes, P.; Sustmann, R. *J. Am. Chem. Soc.* **1984**, *106*, 663. (f) Viehe, H. G.; Janousek, Z.; Merenyi, R. *Acc. Chem. Res.* **1985**, *18*, 148, and references cited therein. (g) Sylvander, L.; Stella, L.; Korth, H.-G.; Sustmann, R. *Tetrahedron Lett.* **1985**, *26*, 749. (g) Pius, K.; Chandrasekher, J. *J. Chem. Soc., Chem. Commun.* **1990**, 41.

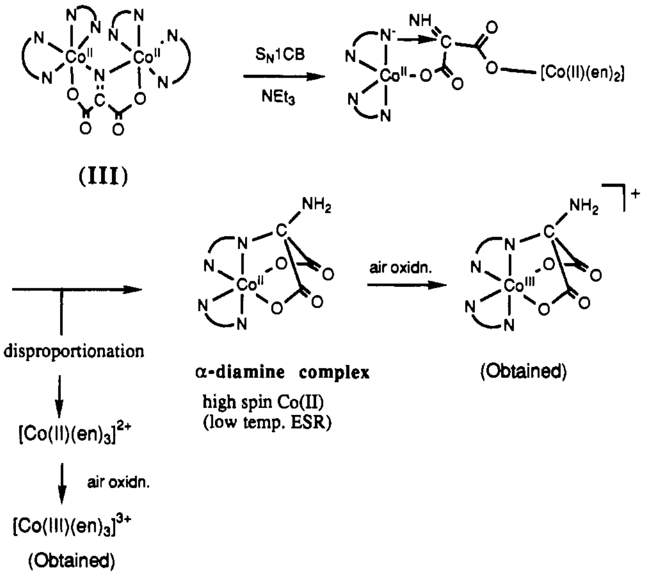
(27) Castro, C. E.; Jamin, M.; Yokoyama, W.; Wade, R. *J. Am. Chem. Soc.* **1986**, *108*, 4179, and references cited therein.

Table I. ESR Parameters of Co(II) Species Generated from the Reactions of *trans*-[$CoCl_2(N_4)$]ClO_4 in Vacuum (Measured at 4.2 K)[a]

	en	2,3,2-tet	3,2,3-tet
complex in MeOH/NEt_3, heated at 65–70 °C	$S = {}^3/_2$ $g_1 = 5.8$, $g_2 = 4.2$, $g_3 = 2.5$	$S = {}^3/_2$ $g_1 = 6.8$, $g_2 = 3.4$ ($g_3 = 2.6$) $S = {}^1/_2$ $g_\perp = 2.29$ ($A_\perp = 40$ G), $g_\parallel = 2.01$ ($A_\parallel = 110$ G)	$S = {}^3/_2$ $g_1 = 7.1$, $g_2 = 4.2$, $g_3 = 2.9$ $S = {}^1/_2$ $g_\perp = 2.29$, $g_\parallel = 2.09$
complex and NH_4AMH in MeOH/NEt_3, heated at 65–70 °C	$S = {}^3/_2$ $g_1 = 6.2$, $g_2 = 4.2$, $g_3 = 2.6$	$S = {}^3/_2$ $g_1 = 5.2$, $g_2 = 4.1$ ($g_3 = 2.3$) $S = {}^1/_2$ $g_\perp = 2.27$ ($A_\perp = 32$ G), $g_\parallel = 1.95$ ($A_\parallel = 109$ G)	$S = {}^3/_2$ $g_1 = 6.0$, $g_2 = 4.3$, $g_3 = 2.9$

[a] All *g* values for high-spin Co(II) species were obtained by computer simulation.

Scheme IV



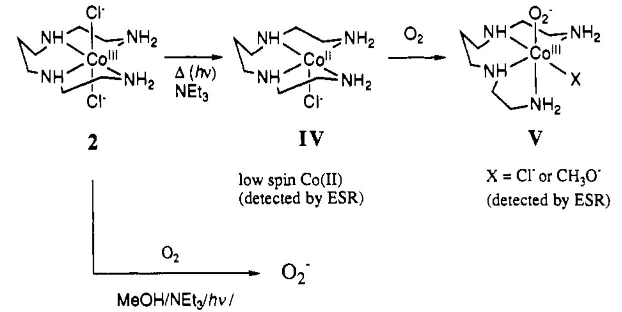
nocarbinyl radical has been postulated as an intermediate which possesses an unpaired electron on the α-position to an amino group. In addition, as reported, an aminocarbinyl radical process must be favored thermodynamically,[30] and α-C–H bond cleavage must be preferred to N–H bond cleavage in a polar solvent.[31] In view of these proposals, the α-carbon radical intermediate is reasonable in the oxidation of AM^{2-}.

3. Formation of α-Diamine Linkage. The α-diamine formation step in this system under anaerobic conditions is represented in Scheme IV.

The bridging imido group in III interacts weakly between two cobalt centers[13] and should dissociate easily in a S_N1CB (S_N1 conjugated base) mechanism.[32] A conjugated base formed at an amino group of an en ligand attacks at the imine carbon to form an α-diamine linkage and another Co(II) complex dissociates to form [$Co(en)_3$]$^{2+}$ by disproportionation. Exposure to the air gives a Co^{III}–α-diamine complex and [$Co(en)_3$]$^{3+}$.

2,3,3-tet System. In this system, as described previously,[9] the α-diamine formation was observed in the reaction of AM^{2-} with **2** in MeOH/NEt_3 in the daylight under air. In contrast, no C–N bond formation was observed between AM^{2-} and **2** in MeOH/NEt_3 under inert atmosphere for 3 h: it gave [Co(AM)(2,3,2-tet)]$^+$ as a main product, in which the AM^{2-} moiety coordinated to the Co(III) center with an amino group and one of carboxyl groups as a bidentate ligand.[9] In addition, α-diamine formation was not observed in the absence of a Co(III) ion.[9] Therefore, it is plausible to consider that the oxidation of AM^{2-} to an iminomalonato intermediate is promoted by a combination of the Co(III) complex and dioxygen.

Scheme V



1. Dioxygen Activation. When only **2** was heated to ca. 70 °C in MeOH/NEt_3 in vacuo, the formation of a low spin ($S = {}^1/_2$) Co(II) complex, $g_\parallel = 1.98$ ($A_\parallel = 120$ G), $g_\perp = 2.20$ ($A_\perp = 49$ G), was indicated by an ESR measurement at 77 K as shown in Figure 4a.[33] When the cooled purple solution of the low-spin complex was exposed to air, the color of the solution turned to brown and the low-spin Co(II) complex readily reacted with dioxygen in the air to form a Co–dioxygen complex adduct, showing $g_\perp = 1.97$ ($A_\perp = 13$ G), $g_\parallel = 2.06$ ($A_\parallel = 21$ G) as exhibited in Figure 4b. Two ESR features of the oxygenated complex V, the smaller hyperfine splitting resulting from ^{59}Co ($I = {}^7/_2$) relative to the unoxygenated complex and $g_\parallel > g_\perp$ strongly suggest that the unpaired electron resides on the dioxygen and not on the cobalt, i.e. Co^{III}–O_2^-.[34]

The absorption spectrum at room temperature of the solution in which **2** was refluxed in MeOH/NEt_3 without NH_4AMH under N_2 atmosphere showed absorption maxima at 561 and around 400 nm (broad shoulder). When the solution was exposed to the air at room temperature, no significant spectral change was observed; particularly no absorption maxima were observed around 300 nm, which is a typical absorption of LMCT assigned to $\pi^*(O_2^{2-}) \rightarrow d(z^2)$ for a μ-peroxo Co(III) complex.[35] The absorption responsible for μ-superoxo Co(III) complexes around 700 nm was not observed.[36] This result shows that no μ-peroxo or μ-superoxo Co(III) complexes are formed at room temperature.

Interestingly, an ESR spectrum measured at 4.2 K of a reaction mixture in which **2** without NH_4AMH was heated at 65–70 °C in MeOH/NEt_3 in vacuo exhibited resonances at $g_1 = 6.8$, $g_2 =$

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(28) Laloo, D. L.; Mahanti, M. K. *J. Chem. Soc., Dalton Trans.* **1990**, 311.

(29) Garcia-Raso, A.; Deya, P. M.; Saá, J. M. *J. Org. Chem.* **1986**, *51*, 4285.

(30) Lewis, F. D.; Correa, P. F. *J. Am. Chem. Soc.* **1984**, *106*, 194.

(31) Lewis, F. D.; Zebrowski, B. F.; Correa, P. F. *J. Am. Chem. Soc.* **1984**, *106*, 187.

(32) Basolo, F.; Pearson, R. G. *Mechanisms of Inorganic Reactions*, 2nd ed.; John Wiley & Sons: New York, 1967.

(33) (a) Schrauzer, G. N.; Lee, L.-P. *J. Am. Chem. Soc.* **1968**, *90*, 6541. (b) Hoffman, B. M.; Diemente, D. L.; Basolo, F. *J. Am. Chem. Soc.* **1970**, *92*, 61. (c) Urbach, F. L.; Bereman, R. D.; Topioch, J. A.; Hariharan, M.; Kalbacher, B. J. *J. Am. Chem. Soc.* **1974**, *96*, 5063. (d) Stevens, J. C.; Busch, D. H. *J. Am. Chem. Soc.* **1980**, *102*, 3285. (e) Sugiura, Y. *J. Am. Chem. Soc.* **1980**, *102*, 5216. (f) Kuwanishi, S.; Sano, S. *J. Chem. Soc., Chem. Commun.* **1984**, 1628. (g) Kohno, M.; Ohya-Nishiguchi, H.; Yamamoto, K.; Sakurai, T. *Bull. Chem. Soc. Jpn.* **1984**, *57*, 932. (h) Bakac, A.; Brynildson, M. E.; Espenson, J. H. *Inorg. Chem.* **1986**, *25*, 4108. (i) Taylor, R. J.; Drago, R. S.; George, J. E. *J. Am. Chem. Soc.* **1989**, *111*, 6610. (j) Bakac, A.; Espenson, J. H. *J. Am. Chem. Soc.* **1990**, *112*, 2273.

(34) See ref 33i,j. See also: (a) Drago, R. S.; Cordon, R. B. *Acc. Chem. Res.* **1980**, *3*, 353. (b) Tovrog, B. S.; Kitko, D. J.; Drago, R. S. *J. Am. Chem. Soc.* **1976**, *98*, 5144.

(35) Pickens, S. R.; Martell, A. E. *Inorg. Chem.* **1980**, *19*, 15.

(36) (a) Bagger, S.; Gibson, K. *Acta Chem. Scand.* **1972**, *26*, 3788. (b) Miskowski, V. M.; Robbins, J. L.; Treitei, I. M.; Gray, H. B. *Inorg. Chem.* **1975**, *14*, 2318.

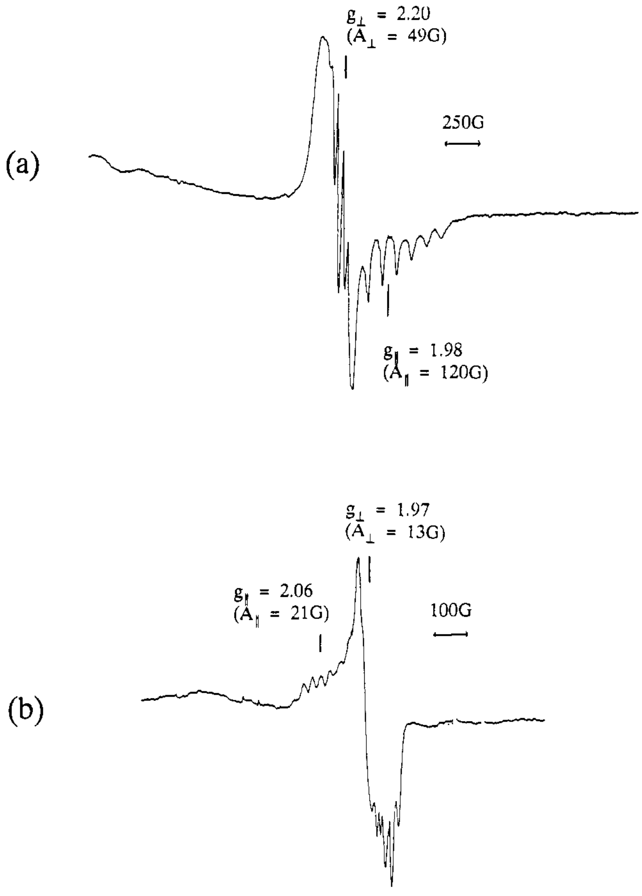

Figure 4. Change of ESR spectra, (77 K) in the 2,3,2-tet system by heat and dioxygen: (a) **2** in MeOH/NEt$_3$ heated in vacuum at 70 °C for 30 min in the daylight; (b) after exposure of solution a to the air. ESR spectrometer conditions: (a) microwave power, 20 mW; modulation, 100 kHz, 4 G; scan range, 2500 ± 2500 G; gain, 2 × 1000; response, 1 s. (b) microwave power, 20 mW; modulation, 100 kHz, 4 G; scan range, 3000 ± 1000 G; gain, 2 × 1000; response 1 s.

3.4 assigned to a high-spin Co(II) species and $g_\perp = 2.29$ ($A_\perp$ = 40G) and $g_\parallel = 2.01$ ($A_\parallel$ = 110G) attributed to a low-spin Co(II) species. This low-spin species shows typical values for a five-coordinated Co(II) complex. The ESR parameters observed at 4.2 K are cited in Table I. However the formation of a high-spin Co(II) complex was observed in the 2,3,2-tet system as shown in Table I; it is assumed that the high-spin species is not essential for the oxidation of AM^{2-} in this system.

When **2** in the absence of NH$_4$AMH was irradiated by a Hg lamp in MeOH/NEt$_3$ under air at −78 °C for 30 min, the ESR spectrum at 77 K showed a resonance at $g_\perp = 2.006$ and $g_\parallel = 2.117$. These values are typical for a free superoxide anion (O$_2^-$).[37] The release of the free superoxide anion was reported in Co^{II}-(tetraphenylporphyrin)/R–SH/O$_2$. In the cobalt–porphyrin system, ET takes place from a low-spin complex to O$_2$ followed by ligand substitution of a formed O$_2^-$ ligand by a thiolate to generate the free O$_2^-$.[38] In the 2,3,2-tet system, O$_2^-$ is released via a photoinductive ligand substitution by d–d transition.[39] This reaction represents a novel reaction pattern for a Co^{III}–O$_2^-$ complex. Moreover, this result strongly suggests formation of a mononuclear superoxo Co(III) complex intermediate for the oxidation of AM^{2-}.

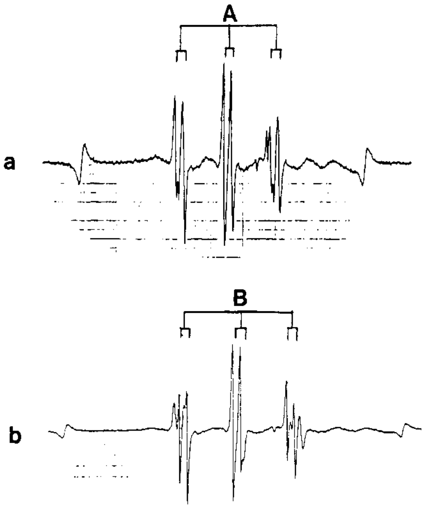

Figure 5. ESR spectra of spin adducts with POBN in the 2,3,2-tet system: (a) **2** and NH$_4$AMH refluxed in MeOH/NEt$_3$ under air in the dark; (b) after irradiation by daylight. ESR spectrometer conditions: (a) microwave power, 20 mW; scan range, 3280 ± 100 G; modulation, 100 kHz, 0.5 G; gain 1 × 1000. (b) microwave power, 20 mW; scan range, 3275 ± 50 G; gain, 6.3 × 100; modulation, 100 kHz, 0.5 G.

The proposed mechanism of the dioxygen activation by **2** is shown in Scheme V. First, an ET from Cl$^-$ to Co(III) ion is promoted thermally and in part photochemically and the homolytic cleavage of the Co–Cl bond to give a five-coordinated low-spin Co(II) complex IV which was observed by ESR spectroscopy. The low-spin Co(II) complex activates dioxygen and undergoes base-catalyzed trans to cis isomerization of the oxygenated complex V.

2. Oxidation of AM^{2-}. An ESR spectrum with POBN as a spin trap for a reaction mixture of **2** and NH$_4$AMH in MeOH/NEt$_3$ refluxing for 30 min in the dark under air showed a doublet of triplets, assigned to an spin adduct of a carbon-centered radical A (POBN spin adduct; a_N = 15.4 G, a_H = 2.5 G, g = 2.01). The spectrum also includes a minute multitude of another doublet of triplets assigned to an oxygen-centered radical B (POBN spin adduct; a_N = 14.9 G, a_H = 2.0 G, g = 1.99). The spin adduct of B increased by daylight, indicating that a photoinduced radical formation should be included as shown in Figure 5. These data suggest that the α-diamine formation also proceeds via the radical mechanism in the 2,3,2-tet system.

When both **2** and NH$_4$AMH in MeOH/NEt$_3$ were heated at 65–70 °C for 3 h, an ESR spectrum at 4.2 K of the reaction mixture changed to show a resonance of a high-spin Co(II) species dominantly at g_1 = 5.2 and g_2 = 4.1 (g_3 = 2.3) and small amounts of a low-spin Co(II) species at $g_\perp$ = 2.27 ($A_\perp$ = 32 G) and $g_\parallel$ = 1.95 ($A_\parallel$ = 109 G). The latter resonance slightly increased its intensity with further heating. Since it has been well-known that a low-spin Co(II) center readily activates dioxygen, these observed Co(II) ions should have been reduced from a starting Co(III) complex with 2,3,2-tet ligand. Moreover, the low-spin Co(II) intermediates should be responsible for the formation of the Co^{III}–O$_2^-$ complex in the presence of dioxygen.

The possibility of extraction of the α-proton by the superoxo ligand is examined by using EHMO calculations on a hypothetical intermediate (VI), assumed to include AM^{2-}, O$_2^-$, and 2,3,2-tet as ligands. It showed that net charges of the α-proton of AM^{2-}, the terminal oxygen atom of the superoxo ligand, and the cobalt center change drastically in accordance with the rotation of AM^{2-} moiety around the coordinating axis. When the α-proton of AM^{2-} came to the nearest position to the terminal oxygen of the superoxo ligand, the net charge of the α-proton showed the highest value, also that of the terminal oxygen atom of the superoxo ligand exhibited the lowest one, and that of cobalt center was reduced. This result indicates that the oxidation of AM^{2-} could occur via the abstraction of α-proton by the superoxo ligand followed by the ET from the α-carbon to the metal center. A proposed in-

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[37] Ohya-Nishiguchi, H.; Yamauchi, J. *Electron Spin Resonance*; Koudan-Sha, 1989; p 158.

[38] Sakurai, H.; Ishizu, K. *J. Am. Chem. Soc.* **1982**, *104*, 4960.

[39] (a) Adamson, A. W. *Coord. Chem. Rev.* **1968**, *3*, 169. (b) Pribush, R. A.; Poon, C. K.; Bruce, C. M.; Adamson, A. W. *J. Am. Chem. Soc.* **1974**, *96*, 3027. (c) Langford, C. H.; Malkhasian, A. Y. S. *J. Am. Chem. Soc.* **1987**, *109*, 2682.

[40] ESR spectroscopy revealed that the Co^{III}–O$_2^-$ complex underwent a homolytic photolysis to form mother Co(II) species as reported in ref 33j.

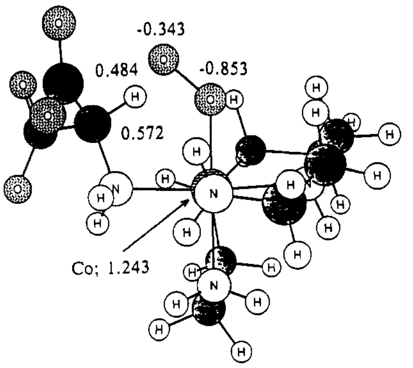
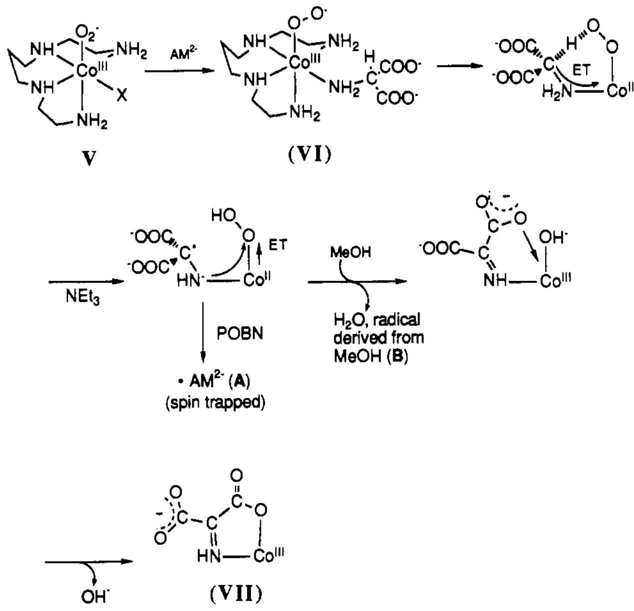


Figure 6. A calculated $Co^{III}-O_2^{-}-AM^{2-}$ intermediate for dehydrogenation of an α-proton of AM^{2-} in the 2,3,2-tet system involving selected net charges.

Scheme VI

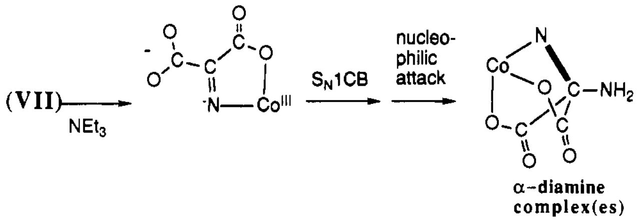


termediate structure is shown in Figure 6.

Another possible oxidation pathway of AM^{2-} is a μ-peroxo mechanism, proposed for the oxidative dehydrogention of coordinated aromatic amines by Martell and co-workers.[41] They referred to the importance of conjugation of imines formed via the dehydrogenation with the aromatic rings. However, the reaction in the 2,3,2-tet system should be considered without the formation of a μ-peroxo intermediate as described above. Moreover, when the μ-peroxo mechanism is adopted, the participation of a solvent, i.e. MeOH, becomes unclear and the μ-peroxo mechanism is in conflict with results of spin trap ESR spectroscopy that indicates the oxygen-centered radical formation. Therefore, the dehydrogenation of AM^{2-} to form an iminomalonato intermediate appears to proceed via the mononuclear $Co^{III}-O_2^{-}$ pathway.

For all reasons mentioned above, the oxidation mechanism of AM^{2-} in the 2,3,2-tet system is proposed as shown in Scheme VI. AM^{2-} coordinates to the oxygenated cobalt center in the amino group at a cis position to a superoxo ligand and is activated by the electron-withdrawing effect of the cobalt center (intermediate VI). The superoxo ligand abstracts the α-proton of AM^{2-} and ET from the α-carbon of AM^{2-} to the cobalt center results in the formation of the α-carbon radical of AM^{2-} and reduction of the metal center. The deprotonation of an amino proton of AM^{2-} takes place prior to the oxidation of AM^{2-} to form an iminomalonato intermediate (VII). A hydroperoxo moiety on the Co(II) center is likely reduced by MeOH and replaced by a carboxyl group of the iminomalonato intermediate.

Scheme VII



3. C–N Bond Formation Step. As shown in Scheme VII, the imine intermediate (VII) undergoes the deprotonation of an active imine proton and a deprotonation imino group dissociates from the cobalt center to become open to the nucleophilic attack of a coordinated and deprotonated amino group (a conjugated base) of 2,3,2-tet ligand. The nucleophilic attack by the amino group of 2,3,2-tet takes place via a S_N1CB mechanism.

4. Reaction in the Presence of *p*-Benzoquinone. The reaction of **2** with NH_4AMH in $MeOH/NEt_3$ in the presence of an excess amount of *p*-benzoquinone upon reflux for 3 h under inert atmosphere gave a mixture of the α-diamine complexes in lower yields (24% total) than those of the reaction under air (ca. 40% total).[9c] In this case, *p*-benzoquinone probably oxidizes AM^{2-} to form the iminomalonato intermediate.

In order to reveal radical intermediates, ESR spectroscopy was examined for the reaction mixtures including **2**, NH_4AMH, and *p*-benzoquinone. An ESR spectrum of a reaction mixture in which **2**, NH_4AMH, and *p*-benzoquinone were refluxed in $MeOH/NEt_3$ for 30 min under N_2 atmosphere showed a resonance having a hyperfine splitting resulting from ^{59}Co ($I = {}^7/_2$) found to be $a_{Co} = 6.3$ G. These results show that *p*-benzoquinone is reduced to form a semiquinone radical interacted with the Co(III) center. The reduction of *p*-benzoquinone should be attributed to the oxidation of AM^{2-}.

The ESR spectrum involving the semiquinone radical observed in this case shows the smaller coupling constant compared with a reported hyperfine coupling constant for (3,5-di-*tert*-butylcatecholato)(3,5-di-*tert*-butylsemiquinone)(bipyridyl)cobalt(III) complex (Co^{III}(DBCat)(DBSQ)(bpy)) found to be 10–11 G.[42] In the DBSQ complex the *o*-semiquinone moiety coordinates to the Co(III) center as a bidentate ligand; however, *p*-semiquinone binds to the metal center as a monodentate ligand. Therefore the difference of the coordination mode causes that degree of interaction between a Co(III) center and an unpaired electron on a radical ligand: a bidentate radical ligand more strongly interacts with the metal center than a monodentate ligand does.

In addition, the ESR spectrum showed a reversible line-broadening depending on temperatures as observed in the Co–DBSQ system.[42] The semiquinone Co(II) complex derived from *p*-quinone undergoes a similar tautomeric hydroquinone–semiquinone interconversion via ligand–metal and metal–ligand ET.

3,2,3-tet System. In this system, the α-diamine formation took place under air similar to the en and 2,3,2-tet systems and also occurred even under an inert atmosphere in $MeOH/NEt_3$ upon refluxing like the en system.[11] It is noteworthy that the C–N bond formation in this system occurred regioselectively depending on both a counteranion and the presence or absence of dioxygen, whereas no selectivity was observed in the 2,3,2-tet system.[9c,11] Although the reaction mechanism in this system is still umbiguous, the following facts have been revealed in connection with other amine systems described above.

1. Reaction under Air. The spin trap ESR spectrum with POBN as a spin trap in $MeOH/NEt_3$ under air upon refluxing for 30 min gave a similar spectrum and showed similar behavior with photoirradiation to those for the 2,3,2-tet system. In the dark, a spin adduct of a carbon-centered radical with POBN having

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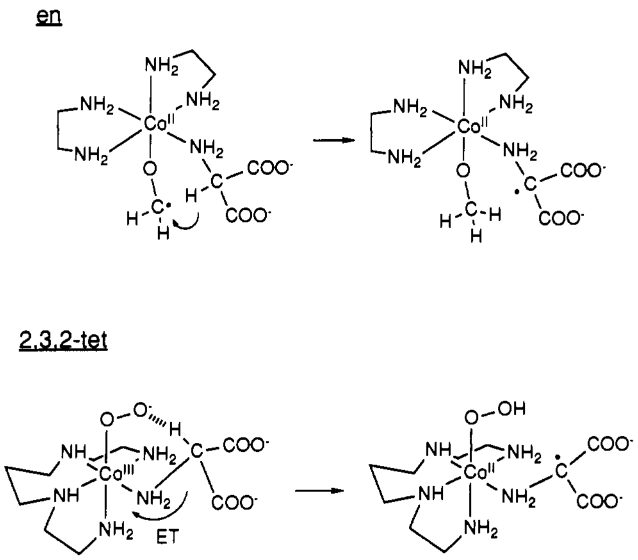
[41] (a) Raleigh, C. J.; Martell, A. E. *Inorg. Chem.* **1985**, *24*, 142; *Inorg. Chem.* **1986**, *25*, 1190. (b) Basak, A. K.; Martell, A. E. *Inorg. Chem.* **1986**, *25*, 1182. (d) Martell, A. E.; Basak, A. K.; Raleigh, C. J. *Pure Appl. Chem.* **1988**, *60*, 1325.

[42] Buchanan, R. M.; Pierpont, C. G. *J. Am. Chem. Soc.* **1980**, *102*, 4951.

Scheme VIII



hyperfine coupling constants C (a_N = 15.3 G, a_H = 2.4 G, g = 2.01) and that of an oxygen centered radical D (a_N = 14.5 G, a_H = 2.06 G, g = 2.01) were observed in the reaction mixture of **3** and NH_4AMH. With irradiation of the sample tube by the daylight, the oxygen-centered radical formation was enhanced. These results should indicate that the α-diamine formation in the 3,2,3-tet system under air occurs through a radical mechanism and a photoinductive dioxygen activation as observed in the 2,3,2-tet system.

2. Reaction under an Inert Atmosphere. When only **3** without NH_4AMH was heated to about 70 °C in MeOH/NEt$_3$ in vacuo for 3 h, ESR spectroscopy indicated the formation of a mixture of low-spin Co(II) and high-spin Co(II) complexes like the 2,3,2-tet system. The low-spin Co(II) species showed a resonance of $g_\perp$ = 2.29, $g_\parallel$ = 2.09 and the high-spin complex exhibited a resonance at g_1 = 7.1, g_2 = 4.2, and g_3 = 2.9. Although the similar hydroxymethylene radical as observed in the en system was not detected, the Co(III) ion in **3** was reduced in MeOH/NEt$_3$.

Interestingly, when both **3** and NH_4AMH were heated to 70 °C in MeOH/NEt$_3$ in vacuo, an ESR spectrum of a reaction mixture only showed a resonance assigned to another high-spin Co(II) species at g_1 = 6.0, g_2 = 4.3, and g_3 = 2.9, and no low-spin species. This complete change of the spin state at the cobalt center was observed in the systems in which the C–N bond formation can take place even under an inert atmosphere via ET from AM^{2-} to a Co(III) ion in a polyamine complex as observed in the en system.

Summary

The C–N bond formation to form an α-diamine linkage between the α-carbon of AM^{2-} and an coordinated amino group of a polyamine ligand is essentially thermal and base-induced. In particular, MeOH is indispensable as a solvent. The conditions demanded for the C–N bond formation depend on each polyamine system; dioxygen is necessary for the reaction in the 2,3,2-tet system, whereas it occurs even under an inert atmosphere in the en and 3,2,3-tet systems.

The Co(III) complexes undergo thermal and/or photochemical reduction to form low-spin or high-spin Co(II) species under basic conditions. The reduction behavior of the Co(III) ions in them is different for each system. In the en system, a base-induced thermal ET from MeOH to the Co(III) center in **1** forms an oxymethylene radical and a high-spin Co(II) complex. In contrast, in the 2,3,2-tet system thermal and photochemical ET causes the formation of a low-spin Co(II) complex which is responsible for dioxygen activation to form a mononuclear superoxo complex.

The α-diamine formation involves the oxidation of AM^{2-} toward an iminomalonato intermediate, and the oxidation process is varied depending on each polyamine system. The difference of the oxidation mechanism of AM^{2-} between the en and 2,3,2-tet systems is illustrated in Scheme VIII. In the en system the intramolecular hydrogen abstraction takes place on the α-hydrogen of AM^{2-} by the coordinated oxymethylene radical to give the α-carbon radical of AM^{2-}. In sharp contrast, in the 2,3,2-tet system, dioxygen is activated to form a superoxo ligand by the reduced cobalt center and the α-carbon radical of AM^{2-} is induced via the α-proton abstraction by the superoxo ligand followed by simultaneous ET from the α-carbon to the cobalt ion.

The bond-forming step probably proceeds via the S_N1CB mechanism, i.e. the deprotonation of a coordinated amino group and dissociation of imino (imido) group of iminomalonato intermediate; the dissociated imino group undergoes a nucleophilic attack of the deprotonated amino group (conjugated base).

When the α-diamine complexes are formed by the reactions under anaerobic conditions, the cobalt center undergoes alteration of the spin state from a d^6 *low-spin state* to a d^7 ***high-spin state*** via ET from AM^{2-}. The complete rearrangement of electronic structure is a requirement for the oxidation of AM^{2-} toward an iminomalonato intermediate by a Co(III) ion. This ET process is reminiscent of a catalytic cycle of the cytochrome P-450 system: the distortion around a low spin ferric resting center converts the spin state into a high-spin ferric state which undergoes ET from cytochrome P-450 reductase.[43] Thus, the steric constraint around a metal center is an important factor for ET to a metal center. Concerning the α-diamine formation between AM^{2-} and cobalt(III)-polyamine complexes, Co(III) ions wearing more *flexible* polyamine ligands (en, tn,[44] and 3,2,3-tet) can undergoes ET to form the α-diamine linkage. In contrast, Co(III) having more *rigid* ligands such as 2,3,2-tet and cyclam[45] cannot perform the ET to oxidize AM^{2-} toward the iminomalonato intermediate.

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(43) Peterson, J. A.; Prough, R. A. Chapter 4 in ref 5c.

(44) tn = 1,3-diaminopropane. When this amine was used as a ligand, the similar α-diamine formation was observed under both aerobic and anaerobic conditions.

(45) cyclam = 1,4,8,11-tetraazacyclotetradecane. In the case of using this amine as a ligand, [Co(glycinato)(cyclam)]$^{2+}$ derived from thermal decarboxylation of AM^{2-} was obtained as a main product without the formation of α-diamine complex under both aerobic and anaerobic conditions.